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Bioassay and alpha spectrometry in indirect monitoring of Spanish workers exposed to enriched uranium

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Workers at risk of exposure to uranium compounds should be monitored and their internal exposure quantified in terms of committed effective dose E(50) in mSv. *In vitro* bioassay methods can quantify uranium in urine and faeces at low activity levels. Alpha spectrometry (AS) is the most common method used for monitoring alpha-emitting radionuclides in internal dosimetry services. It provides isotopic information and low minimum detectable activity (MDA) values (≤0.50 mBq per sample). This study reports the results of a five-year monitoring of workers exposed to uranium at a Spanish Juzbado facility, which produces nuclear fuel elements enriched with up to 5 % of ^{235}U. Monitoring included about 100 workers per year, most of whom had worked at the facility for more than 10 years before the individual monitoring programme was established. We analysed nearly 550 samples of more than 200 workers over five years. The obtained results indicate that workers were adequately protected from uranium exposure through inhalation and had an acceptably low chronic intake at the facility.

KEY WORDS: indirect bioassay; internal dosimetry; urine samples; uranium isotopes

The Juzbado facility of ENUSA Industrias Avanzadas S.A. (ENUSA) located in Salamanca (Spain) manufactures nuclear fuel elements for Spanish nuclear power plants. Its annual production capacity is 500 t of up to 5 % ^{235}U-enriched uranium (1). The manufacturing process puts more than 200 workers at risk of internal exposure, which is why they need to be monitored for internal exposure. Since 2014, CIEMAT has been assessing internal dosimetry of permanent staff of the facility (around 100 workers per year) in terms of committed effective dose E(50) in mSv. As *in vivo* methods are not always adequate for quantifying exposure to alpha emitters because their detection limits are too high (2), *in vitro* bioassay methods are preferred, as they quantify uranium in urine at low activity levels (3, 4). This is particularly relevant for radionuclides incorporated into the body as insoluble compounds through inhalation, because in this case the urinary excretion of uranium isotopes is low and slow (5).

The CIEMAT Bioelimination Laboratory uses three indirect methods of quantifying uranium: kinetic phosphorescence analysis (KPA), inductively coupled plasma-sector field mass spectrometry (ICP-SF-MS), and alpha spectrometry (AS). KPA or ICP-MS are employed for screening workers at risk of internal contamination by natural uranium. If the results obtained with these methods are above detection limit (0.10 µg/L for KPA and 0.004 mBq/L (^{238}U) for ICP-MS), an isotopic analysis with AS is the next step. It is the reference and most common method used for monitoring alpha-emitting radionuclides in internal dosimetry services, as it provides isotope information and has a low minimum detectable activity (MDA) ≤0.50 mBq per sample. However, it takes tedious chemical processing to isolate actinides from inactive substances and separate them from other radioisotopes which may interfere with AS measurement. It also takes long counting times (3–5 days) (3–7).

The aim of this study was to establish potential internal exposure of workers at the Juzbado facility to enriched uranium compounds by monitoring about 100 workers per year over five years (2014–2018). Most of these workers had been working at the facility for more than 10 years before the individual monitoring program was established. We applied a new method developed for the separation and analysis of uranium isotopes (^{238}U, ^{236}U, ^{235}U, and ^{234}U) in urine samples using ion exchange chromatography and alpha spectrometry. It is an adaptation of an older procedure used at our laboratory (8), and its main novelty is that it can be applied for chronic inhalation scenarios. Earlier measurement methods (such as *in vivo* whole body counter and kinetic phosphorescence analysis in urine) were less sensitive and used only for accidental exposures or when activity was above the detection limit, in which case they were followed up by AS to confirm contamination. Since 2014, CIEMAT has established an improved radiochemical procedure for individual monitoring of Spanish workers exposed to enriched uranium for 10–30 years as part of routine internal exposure monitoring programme (9). The

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accuracy and reliability of this analytical procedure have been tested and validated at international intercomparison exercises. CIEMAT Bioelimination Laboratory also has the ISO/IEC 17025 accreditation since 2012 (10, 11).

This report presents the activity results (mBq/day) of a five-year monitoring of urine samples taken from the Juzbado workers, which reflect their chronic intake (internal doses) through inhalation.

METHODS AND VALIDATION

Chronically inhaled internal doses are assessed following the International Commission on Radiological Protection (ICRP) recommendations and biokinetic models (12, 13). Routine monitoring of workers exposed to enriched uranium (3–5 %) assumed only inhalation intake and chronic exposure. The intake scenario assumed exposure to uranium oxides with type S of solubility and a default particle size of 5 µm of activity median aerodynamic diameter (AMAD) (9). For that purpose 24-hour urine samples were required, initially at annual frequency. New employees gave a urine sample before exposure began for background subtraction.

Samples were collected and creatinine content was determined according to the method described by Young (14), based on the formation of a coloured complex with a basic picrate solution. Sample volume was corrected assuming an average creatinine excretion rate of 1.7 g/day for men and 1.0 g/day for women (15) to normalise radionuclide amount measured in the sample to the equivalent of a true 24-hour collection.

Analytical procedures

All chemicals used were of analytical grade quality and solutions were prepared with deionised water. Anion exchange resin AG1-X8 (100–200 dry mesh, chloride form) was purchased from Bio-Rad Laboratories (Irvine, CA, USA). Radionuclide reference solution used as tracer (^{232}U) was metrologically traceable to the Ionizing Radiation Metrology Laboratory (LMRI) of CIEMAT.

Figure 1 shows a flow chart of the analytical procedure used to determine uranium isotopes in urine, which consists of three main preparation steps (pre-concentration step, radiochemical separation, and electrodeposition) prior to AS.

Pre-concentration step

The whole sample was transferred into a glass beaker, acidified with concentrated HNO_3 (65 %), and 1 mL of concentrated phosphoric acid (85 %) was added to initiate the process. Isotopic tracer (^{232}U) was added to quantify recovery of the analytical procedure. Sample and tracer were equilibrated by heating and magnetic stirring in a water bath at 80 °C for at least 30 min. Uranium isotopes were then co-precipitated with calcium phosphate in ammonia with continuous stirring for 1 h. The precipitate was left to settle overnight and was then separated by decanting and centrifugation. The supernatant was discarded and the precipitate centrifuged, washed with 2 mol/L of HNO_3 and finally evaporated to dryness. The residue was then wet ashed up to five times with 3–5 mL of concentrated HNO_3 at 300 °C. Finally, the obtained residue was dissolved in 50 mL of HCl (10 mol/L).

Radiochemical separation

Uranium was isolated by anion exchange chromatography using AG1-X8 resin. About 8–10 g of resin (suspended in H_2O) was transferred into a glass column and rinsed with 2x30 mL of 10 mol/L HCl. The sample solution was then loaded in the column, and the resin washed with 4x25 mL of 10 mol/L HCl. Uranium isotopes were then eluted with 4x20 mL of 0.5 mol/L HCl.

Electrodeposition

The uranium fraction was evaporated to dryness and prepared for alpha particle counting by electrodeposition following the procedure described by Hallstadius (16).

Alpha spectrometry

Alpha spectra were measured with an integrated Canberra Alpha Analyst instrument (Model 7200) (Meriden, CT, USA) equipped with passivated implanted planar

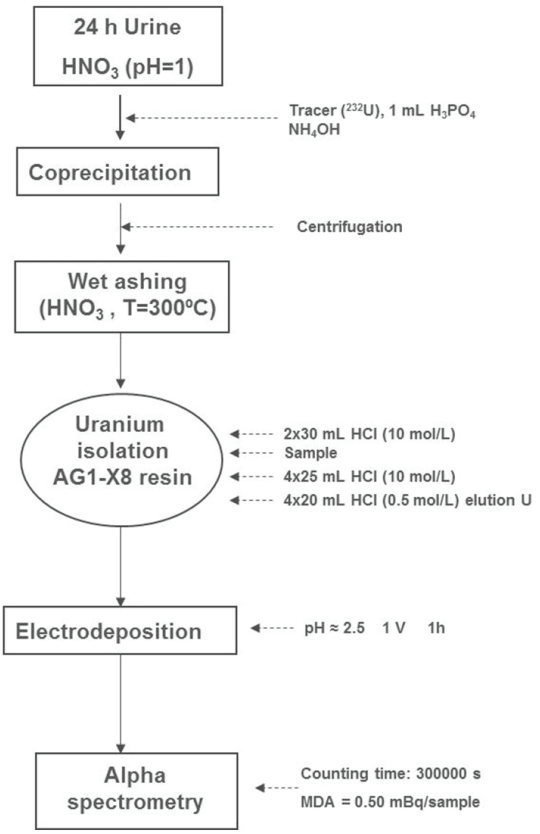

Figure 1 Flow chart of the analytical procedure for the measurement of uranium isotopes in 24-hour urine samples

silicon detectors with a 450 mm^2 active area and full width at half-maximum (FWHM) alpha resolution of 18 KeV at 5.48 MeV.

Figure 2 shows a typical spectrum with enriched uranium isotopes (the ^{232}U peak is due to the tracer added). The typical energy resolution of a monoenergetic (or nearly monoenergetic) peak in the alpha spectrum in urine samples ranged between 20 to 30 KeV.

Internal dose assessment

The committed effective dose E(50) was calculated using Integrated Modules for Bioassay (IMBA) internal dosimetry software (17) and applying IDEAS Guidelines (General guidelines for the estimation of committed effective dose from incorporation monitoring data) (18) together with the methodology described in ISO 27048 (19) and ISO 16638-1 (5) standards for the estimation of uncertainty and the calculation of intake, including the verification of the "goodness of fit" to confirm that experimental data follow the prediction of the excretion model for the intake scenarios.

Quality assurance of the analytical method

The complete method was validated and uncertainty estimated according to accreditation requirements (20). Furthermore, the whole procedure and its results underwent quality assurance through participation in intercomparison exercises. Every year, the CIEMAT laboratory participates in different intercomparison exercises organised by the German Federal Office for Radiation Protection BfS (Bundesamt für Strahlenschutz) (21) and the French association PROCORAD (Association pour la Promotion du Contrôle de Qualité des Analyses de Biologie Médicale en Radiotoxicologie) (22).

Table 1 shows the results validated by the BfS exercise "BfS-Rv-2015-U-nat" in 2015 and PROCORAD intercomparison exercise "Uranium in Urine Exercise" in 2018. Bias and Z-score were within the confidence interval defined by ISO 28218 (23) [-25%, +50% and ≤2, respectively].

RESULTS AND DISCUSSION

From 2014 to 2018, nearly 550 urine samples (between 77 and 133 a year) from more than 200 workers (about 100 a year) were analysed with this radiochemical method. The obtained tracer recoveries in Table 2 show the reliability and robustness of the whole procedure. Thanks to these average recoveries, counting time of 300.000 s, counting efficiency of 26–31 %, and typical background range of 0–4 counts, MDA was lowered to 0.05–0.19 mBq per sample. The need for lowering MDA is the consequence of extremely low daily urinary excretion rates for uranium radionuclides.

Activity results showed great variability, from values below MDA to activity rates of 18.89 mBq/day. However, most were below 5 mBq/day (Figure 3). The most significant average activity of ^{234}U of around 2–3 mBq/day remained stable throughout the five years of monitoring. Only 5.6–17.7 % of the analysed samples had activity higher than 5 mBq/day. More precisely, it was stable at about 7 mBq/day. For this reason, routine monitoring programme

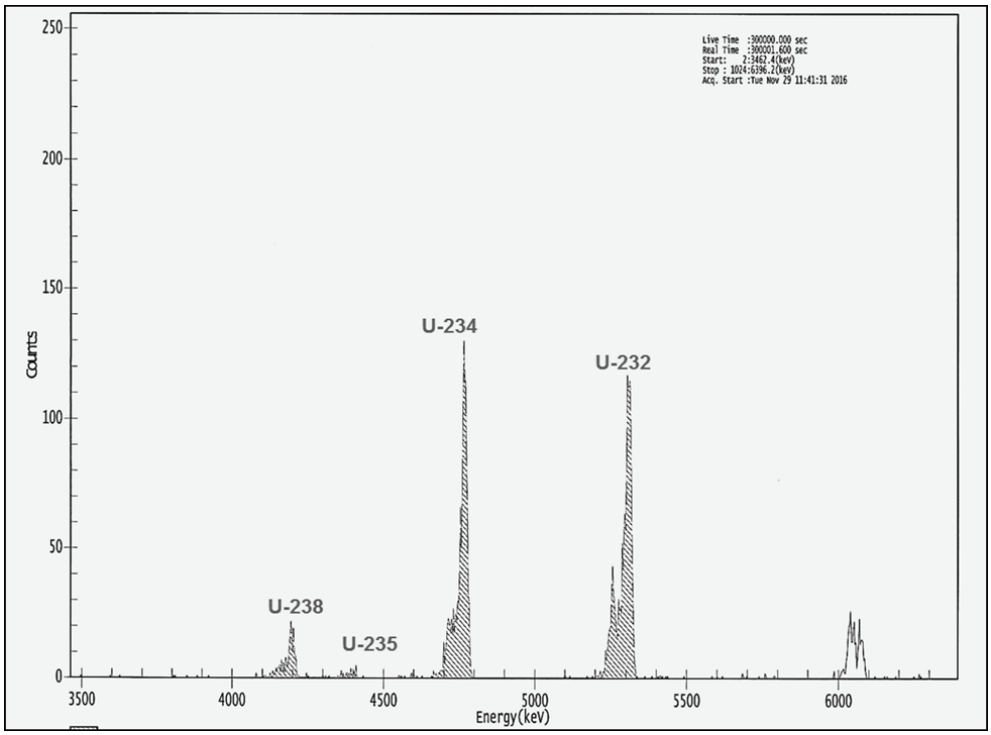

Figure 2 Typical alpha spectra for enriched uranium isotopes in a 24-hour urine sample

Table 1 Uranium isotope target values and activity concentrations measured in the 2015 Bfs sample and in the 2018 PROCORAD samples

BfS exercise (2015)			**mBq/L**		
Sample	**Nuclide**	**Target value**	**Measured value**	**Bias (%)**	**Z-score**
A	^{234}U	49.9±1.57	45.5±1.66	-9	0.442
A	^{235}U	2.34±0.16	2.33±0.22	0	<0.10
A	^{238}U	50.9±1.35	46.1±1.49	-10	0.478
PROCORAD exercise (2018)			**mBq/sample**		
Sample	**Nuclide**	**Target value**	**Measured value**	**Bias (%)**	**Z-score**
A	^{234}U	143.0± 11.3	140.0±14.0	-2	-0.2
	^{235}U	6.87±0.54	6.49±0.78	-6	-0.3
	^{238}U	142.0± 9.4	140.0±15.4	-1	-0.2
B	^{234}U	37.1±3.74	34.0±4.42	-8	-0.8
	^{235}U	1.81±0.18	1.49±0.22	-18	-1.0
	^{238}U	36.7±3.34	34.2±4.44	-7	-0.9

Table 2 Uranium activity (^{234}U) findings in the urine samples of the Juzbado workers

Year	**Average recovery (%)**	**Total samples**	**Average activity (mBq/day)**	**Average activity >5 mBq/day**
			>MDA (0.50 mBq/sample)	
2014	78	77	3.25±0.47 (n=76)	6.97±0.79 (n=14)
2015	69	98	2.56±0.48 (n=90)	7.86±0.98 (n=11)
2016	81	126	2.47±0.38 (n=110)	8.37±0.91 (n=15)
2017	83	133	2.02±0.34 (n=124)	7.41±0.86 (n=8)
2018	81	114	1.98±0.31 (n=105)	7.22±0.78 (n=7)

frequency for the most exposed workers (receiving 5 mSv/year or more) was doubled from annual to biannual.

Furthermore, these monitoring findings suggest that the workers at the Juzbado facility were effectively protected from uranium exposure through inhalation and had an acceptably low chronic intake.

Based on the ^{234}U alpha spectrometry results with MDA of 0.5 mBq/day) and the isotopic composition of enriched uranium of around 4%, the committed effective dose E(50) for a worker who exposed to chronic inhalation for 10 years when the first 24-hour urine sample is collected was calculated to be around 0.3 mSv/year.

CONCLUSIONS

The analytical methodology developed by CIEMAT for *in vitro* bioassay of enriched uranium in urine is adequate to describe chronic inhalation exposure (routine monitoring) and accidental acute exposure. The obtained results prompted us to double the frequency of routine monitoring to biannual for samples of the most exposed workers at the facility. However, for most of the workers the daily activity rate of uranium isotopes in urine samples over five years confirmed low level chronic intakes and verify a correct protection of workers.

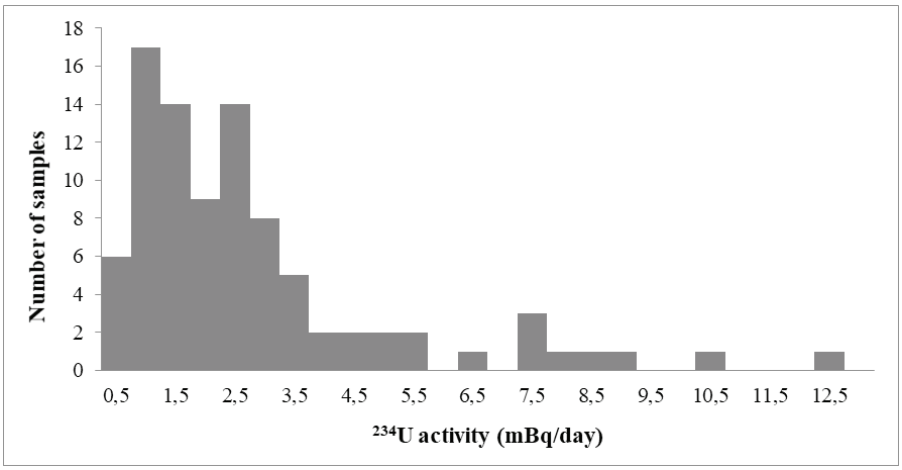

Figure 3 Distribution of ^{234}U activity (mBq/day) in 2015

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Primjena bioeseja i alfa-spektrometrije za neizravno praćenje španjolskih radnika izloženih obogaćenom uraniju

Radnici koji su izloženi riziku od izloženosti spojevima s uranijem trebaju se pratiti i njihova unutrašnja izloženost mjeriti pomoću očekivane efektivne doze E(50) izražene u mSv. Uranij se može kvantificirati u mokraći čak i pri vrlo niskim razinama aktivnosti pomoću bioesejnih metoda *in vitro*. Najčešća metoda koja se rabi u internoj dozimetriji za praćenje/nadziranje razina radionuklida koji emitiraju alfa-čestice jest alfa-spektrometrija. Njome se identificiraju izotopi i može otkriti nisku minimalnu aktivnost (engl. *minimum detectable activity*, MDA) (≤0.50 mBq po uzorku). Ovdje donosimo rezultate petogodišnjega praćenja radnika izloženih uraniju u španjolskoj tvornici sastojaka za nuklearno gorivo Juzbado, u kojoj se sastojci obogaćuju izotopom ^{235}U do udjela od 5 %. Pratilo se oko 100 radnika na godinu, a većina njih je radila u tvornici više od deset godina prije nego što je uveden program praćenja. Ukupno je u pet godina analizirano gotovo 550 uzoraka mokraće oko 200 radnika. Dobiveni rezultati upućuju na to da su radnici dobro zaštićeni od izloženosti uraniju udisanjem te da je kronični unos uranija u tvornici na prihvatljivo niskoj razini.

KLJUČNE RIJEČI: interna dozimetrija; izotopi uranija; neizravni bioesej; uzorci mokraće